The use of lead dodecanoate as an environmentally friendly coating to inhibit the corrosion of lead objects: comparison of three different deposition methods

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Abstract An aqueous sodium dodecanoate solution has been used for the formation of a protective coating for lead. Three deposition methods have been compared: immobilization using cyclic voltammetry, immersion and amperometry. Apart from this, we tested a reduction pretreatment of the lead surface (−1.5 V during 600 seconds) in order to obtain a more reproducible coating, resulting in a better corrosion protection behavior. The corrosion inhibition properties were examined using potentiodynamic polarization curves and electrochemical impedance measurements in a standard corrosive environment.

Keywords Lead conservation; sodium dodecanoate; corrosion inhibition; deposition methods; cultural heritage

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1. Introduction

Potential countermeasures against the corrosion of organ pipes and other historical lead, lead-tin and other lead alloy objects are commonly based on two strategies: on the one hand, the change of the nearby environment and/or on the other hand, the development and the application of a protecting coating, which should ideally be stable, reversible, cheap and aesthetically justified [1].

An interesting candidate for a protective coating has been found in the deposition of saturated linear monocarboxylates of the type $CH_3(CH_2)_{n-2}COONa$ (n = 7-11), hereafter called NaC_n. An initial study by Rocca et al. [2] showed that the immersion of lead metallic objects in NaC_n results in their protection due to the growth of a layer consisting of a crystalline lead monocarboxylate complex $(CH_3(CH_2)_{n-2}COO)_2Pb$, hereafter called $Pb(C_n)_2$. The production of the coating relies on an unassisted formation of lead ions (1) followed by a passivation mechanism (2) according to the following reactions in a neutral solution:

$$Pb + \frac{1}{2}O_2 + H_2O \rightarrow Pb^{2+} + 2OH^- \quad (1)$$

$$Pb^{2+} + 2L^- \rightarrow PbL_2 \qquad \text{with} \qquad L^- = CH_3(CH_2)_{n-2}COO^- \quad (2)$$

This process is slow and depends significantly on the initially polished lead surface [2-3].

In our previous work [4], cyclic voltammetry was used to deposit a lead dodecanoate $Pb(C_{12})_2$ coating. The data initially show an oxidation and reduction peak due to, respectively, the lead dissolution and the lead deposition. After the first scan, a very low passivation current was reached, which is probably a result of the fact that the active reaction sites at the surface are blocked at higher positive potentials. This implies that lead corrosion products are no longer formed.

In this study we continue this research by making a comparison between three deposition methods: immobilization using cyclic voltammetry, immersion and amperometry. Apart from

this, a reduction pretreatment of the lead surface (−1.5 V during 600 seconds) in the sodium dodecanoate solution is tested in order to obtain more reproducible coatings, thereby resulting in a better corrosion protection behavior [5].

In a first stage, the influence of an initial reduction step is studied. Secondly, the coatings are tested for their inhibition effect using electrochemical impedance measurements and potentiodynamic polarization curves in a standard corrosive environment. The lead dodecanoate coatings are characterized on the basis of visual aspects and using electrochemical impedance measurements.

2. Experimental methods

2.1. Materials

A 0.05 mol L^{-1} inhibitor solution was prepared by dispersing 1.252 g of dodecanoic acid (Fluka, Belgium, 98%) in 250 mL deionized water and by subsequently neutralizing the obtained suspension with a 0.25 mol L^{-1} NaOH solution. The addition of NaOH helps the dissolution of the dodecanoic acid (HC_{12}), which is only slightly soluble in water. NaOH should be added until right before the calculated equivalence point (98 % moles of NaOH compared to those of dodecanoic acid), reaching a pH value around 9. This procedure allows us to avoid formation of hydroxide ions, which can easily lead to the formation of lead hydroxides and lead oxides. The initially turbid solution was heated to 25-30 °C and stirred during 1 hour.

The corrosion resistance of the prepared coatings was tested in an ASTM D 1384-87 solution containing 148 mg L^{-1} Na_2SO_4 (Sigma Aldrich, USA), 138 mg L^{-1} $NaHCO_3$ (Sigma Aldrich, USA) and 165 mg L^{-1} NaCl (Sigma Aldrich, USA) [6]. The alkaline mixture represents an environment that simulates typical atmospheric corrosion on lead objects [7]. All reagents were of analytical grade.

2.2. Experimental procedure

The cyclic voltammetry, amperometry and pretreatment measurements were performed using a PGSTAT 100 potentiostat/galvanostat, while the impedance measurements were performed using a PGSTAT20 instrument with a FRA2 frequency response analysis module (both ECO Chemie, The Netherlands). Measurements were controlled by the GPES/FRA 4.9.005 software package.

For all experiments a three-electrode system in a glass cell was used. The set-up consisted of a saturated calomel reference electrode (SCE) containing two compartments (Radiometer Analytical, France), a counter carbon electrode and a polished embedded lead working electrode. The working electrodes were made out of a lead rod (Goodfellow, purity 99.99 %) encapsulated in an epoxy resin. The lead electrodes have a surface with respectively 2 and 6 mm end diameters exposed to the corrosive electrolyte. All fitted impedance and current values were normalized using the surface area of the electrode under study.

The lead electrodes were pre-treated by mechanical polishing, according to the following protocol: freshly made electrodes were first roughly polished on a wetted silicon carbide paper of grit P600. To gain a smooth surface, a silicon carbide paper of P1200 grit was used subsequently. Thereafter, the surface was fine-polished during 1 minute using a cloth (12" micro cloth PSA 10/PK, Buehler) with alumina powder of 1 μm particle size (Buehler, USA) dissolved in isopropanol (Sigma Aldrich). Consequently, the electrode was rinsed with isopropanol and cleaned in an ultrasonic bath containing isopropanol for 30 seconds. The last step of the procedure consisted of polishing the cleaned electrodes by pressing them on a bare cloth (12" microcloth PSA 10/PK, Buehler) with if necessary a small amount of isopropanol. At the end, a shiny blue-white surface was obtained containing a minimal number of defects.

2.3. Deposition procedures

Table 1 shows the different deposition procedures used to apply a lead dodecanoate coating on the lead electrode surfaces. All procedures were carried out in a 0.05 mol L^{-1} sodium dodecanoate solution. The cyclic voltammetric procedure (CV), as described by us previously [4], deposits the coating by recording 5 consecutive scans between −1.3 and 1.5 V vs SCE at a scan rate of 50 mV s^{-1}. The amperometry procedure (AMP) continuously oxidizes the surface to form lead ions at a constant potential around the low passivation current after the lead oxidation peak in the cyclic voltammogram (i.e. 0.2 V vs SCE during 2000 s). The IMM procedure is based on immersing the lead electrode in the solution during 2000 seconds. Procedures AMP_IR and IMM_IR include a pretreatment step in the form of a cathodic polarization procedure (−1.5 V vs SCE during 600 s) to reduce all previously formed corrosion products present at the surface. The pretreatment step will be referred to as 'initial reduction step or IR'. The cyclic voltammetry procedure does not need an initial reduction step because the lead surface is already reduced during the first backward scan.
After treatment the samples were photographed using a Nikon SMZ800 optical microscope equipped with a Nikon Digital Sight system.

2.4. Corrosion testing procedure

After the deposition, the lead dodecanoate coatings were rinsed in distilled water and air-dried. Consequently the corrosion resistance of the layers was analyzed using linear polarization voltammetry and electrochemical impedance spectroscopy. The potentiodynamic polarization curves were recorded in a potential window of −0.25 V to 1.3 V vs E_{corr} (OCP) with a scan rate of 1 mVs^{-1}, while the electrochemical impedance spectra were acquired within a 1 MHz - 10 Hz frequency range, applying at the corrosion potential a 10 mV

sinusoidal AC perturbation. The frequency range 1 MHz to 1 Hz was distributed logarithmically across the first 120 points in each spectrum and the range 1 Hz – 0.01 Hz across the final 10 points.

3. Results and Discussion

3.1. Influence of an initial reduction step on the corrosion inhibition

Figure 1 shows the electrochemical impedance measurements of a bare lead surface and of a lead dodecanoate modified lead surface (AMP_IR) with and without (AMP) the initial reduction step. The impedance plot of the coating formed by performing an initial reduction step shows higher absolute impedance values, which means that the corrosion resistance of the coating is higher. Furthermore, comparing both coated surfaces with the bare lead surface, we can see that an initial reduction step improves the corrosion resistance of the layer by a factor 2. Indeed, the impedance values of the AMP_IR sample over the chosen frequency range is almost double compared to the AMP sample, taking into account the impedance of the bare lead sample in Figure 1. Testing the initial reduction on lead dodecanoate modified lead surfaces using the IMM and IMM_IR procedures, we obtained similar results. The initial reduction step has consequently a good influence on the formation and the corrosion resistance of the coating layer.

3.2. Influence of the different deposition methods upon the corrosion resistance

3.2.1. Qualitative analysis

3.2.1.1. Analysis of the phase angle vs frequency plots

Figure 2 shows the electrochemical impedance plots (A–B) and the potentiodynamic polarization curves (C) of a bare and coated lead electrodes in an ASTM solution. The electrodes were coated using the procedures CV, AMP_IR and IMM_IR in a NaC_{12} solution

as described in Table 1. The phase angle versus frequency plot (Figure 2A) of the bare lead sample shows in the capacitive quadrant two loops (one half loop) and therefore two well-defined time constants: one at around 10^5 - 10^6 Hz, attributed to the charge transfer process and to the corrosion products formation, and the other one around 10 - 10^2 Hz, due to the diffusion of the electrolyte through the corrosion layer [8].

The phase angle versus frequency diagram for the AMP_IR sample looks very similar to that of the bare lead surface. The increase (with respect to the x-axis or frequency axis of the curve) and the broadening of the loop, in comparison to the untreated surface, validate a slightly higher corrosion resistance of the AMP_IR treated surface compared to the polished bare lead surface. The fact that the characteristic frequencies of the time constants τ of AMP-IR sample are the same as the blank, evidences the presence of a defective lead dodecanoate layer with a low corrosion resistance [8].

The plots of the IMM_IR and CV samples show, however, a very broad phase distribution in the low frequency range (only one time constant), which indicates that the complete surface is covered and protected by the deposited lead dodecanoate coating due to more constant phase values closer to a pure capacitance. The high frequency time constant remains the same compared to the bare lead, but shows a much higher phase angle value in the capacitive quadrant. A possible explanation for this second time constant could be a very small corrosion process on top of the protecting layer without actually destroying the coating. Sekine et al. [9] observed a linear relationship between the frequency at maximum phase angle $f_{\theta max}$, which can be measured easily, and the coating resistance and stated the $f_{\theta max}$ could serve as a criterion for the coating quality. Following this reasoning, it can be seen that the immersion method using the initial reduction procedure produces a somewhat more corrosion resistant layer compared to the cyclic voltammetry method.

3.2.1.2. Analysis of the impedance vs frequency plots

Comparing the impedance versus frequency plots (Figure 2B), one can conclude that the impedance points for the treated surfaces are higher compared to those of the bare surface. The plots for the bare surface and the AMP_IR samples show a large plateau in the 10^4 - 10^5 frequency range, which implies major coating damage. The immersion and cyclic voltammetry plot, on the other hand, show only a frequency-independent plateau at low frequencies, which means the electrolyte can penetrate the coating, but no corrosion process takes place at the lead/coating interface [10]. Grandle et al. [11] found that the maximum impedance at low frequency, Z_{max}, is the most useful and reliable parameter to evaluate coatings. Following this reasoning, we can conclude that the immersion method gives the best result, followed by cyclic voltammetry and amperometry.

3.2.1.3. Analysis of the potentiodynamic polarization plots

The potentiodynamic polarization plots recorded in the ASTM environment in Figure 2C show a shift of the anodic polarization curve to much lower current density values (more than a factor 10 for CV and IMM_IR) compared to that of the untreated bare lead surface. This phenomenon can be explained by the inhibition effect of the lead dodecanoate coating, which influences the dissolution process of the lead [12]. The potendiodynamic polarization curve of the IMM_IR sample shows a lower current density and a higher corrosion resistance compared to the other two, which confirms our EIS measurements.

After the dodecanoate modification, we observe that the lead corrosion potential E_{corr} in the ASTM solution becomes more positive than the one of the bare lead surface. This considerable shift of the OCP by ca. 0.068 V to more positive values can be explained by considering a lead dodecanoate film. This dodecanoate anion inhibitor causes a reaction with

the lead metal and inactivation and passivation of the surface due to the hydrophobic character of the tail. As a result a decrease is observed in the surface area in the aqueous ASTM environment [3,13].

3.2.2. Quantitative analysis

The above-mentioned data were fitted in order to predict the corrosion resistance and corrosion rate of the lead dodecanoate coatings deposited using three deposition methods.

3.2.2.1. Electrochemical impedance data

The spectra were simulated using the equivalent electric circuits shown in Figure 3. Figure 3A shows the electric circuit for a defective coating. This EC was characterized by R_u in series with a R_{pore} - C_{coat} parallel combination and a second R_{ct} - C_{dl} parallel combination in series with R_{pore} [8, 14]. The circuit in Figure 3B is characterized by a R_{ct} - C_{dl} parallel combination in series with a R_u, which was used for protective coatings. To make sure the single Nyquist semicircle responses from the Randles circuit are due to the corrosion on the lead surface, the influence of the perturbing voltage on the impedance plot of a lead dodecanoate layer was studied. Figure 4 shows that the Nyquist semicircle decreases when using a higher perturbing voltage (50 mV) which can be explained by assuming that the semicircle is associated with the corrosion cell. The latter means that an increase in the perturbing voltage causes a decrease in the charge transfer resistance [15].

Both circuits in Figure 3 show CPE (constant phase elements) instead of pure capacitances in order to take into account the non-ideal behavior of the lead dodecanoate film:

$$Z_{CPE} = \left[C(j\omega)^n \right]^{-1} \tag{3}$$

where C is the CPE constant, n is the CPE exponent which can be used as a gauge for

heterogeneity with $0 \leq n \leq 1$, $j = (-1)^{1/2}$, $\omega = 2\pi f$ with f the frequency in Hz and Z is the impedance value of the constant phase element [8, 16]. Afterwards, the CPE values of the experimental fitting can be converted into capacitances (approximated values). The inhibition efficiency can be subsequently calculated from the experimental impedance measurements using the following relationship [10]:

$$IE\ (\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} . 100 \quad (4)$$

where R_{ct} and R^0_{ct} are the charge transfer resistances in the presence and absence of the dodecanoate inhibitor, respectively.

Table 2 shows the extracted EIS parameters for the different lead dodecanoate coatings plotted in Figure 2. The data show that the deposition method has a large influence on the corrosion resistance. The charge transfer resistance R_{ct} value of the layer increases depending on the method (Table 3), because a larger area of the surface is blocked by the lead dodecanoate coating. The data also reveal that the charge transfer resistance, R_{ct}, and the double layer capacitance, C_{dl}, vary in inverse proportion, which can be attributed to the formation of a protective layer [17]. Following this reasoning, we can conclude the immersion method leads to the most corrosion-resistant layers, followed by cyclic voltammetry and finally amperometry. The amperometric deposition shows an increase in pore resistance with respect to the bare lead surface, because a film prevents some of the electrolyte of reaching the bare lead surface.

The formation of a more corrosion resistant layer using the immersion method compared to cyclic voltammetry can be easily explained, because this method does not force the deposition by applying a certain voltage. The immersion allows the slow formation of lead dodecanoate complexes and the production of well-shaped and ordered crystals on the lead surface [18-19]. Well-ordered and better formed crystals can protect the bare lead surface much better against corrosion attacks. Cyclic voltammetry and amperometry oxidize the lead surface to form lead

ions and forces a fast deposition. Thanks to the cyclization the lead dodecanoate molecules can reorient and form better ordered crystals, which provides a more corrosion-resistant layer using cyclic voltammetry compared to amperometry.

3.2.2.2. Potentiodynamic polarization data

The electrochemical polarization parameters for the lead dodecanoate coatings deposited using different methods in an ASTM solution are listed in Table 3. The parameters include the corrosion potentials E_{corr}, the current densities i_{corr} and the anodic (β_a) and cathodic (β_c) Tafel constants as well as the inhibition efficiencies IE (%). The inhibition efficiency based on the Tafel measurements is calculated using the following relationship [9]:

$$IE\ (\%) = \frac{1-i_{corr}}{i^0_{corr}}\ .100 \qquad (5)$$

Data for the corrosion current density, i_{corr}, values, show lower values (ca a factor 50) for the coated surfaces in comparison to the bare lead surface. This significant decrease confirms the presence of a protective layer, thereby confirming the EIS measurements.

Table 3 shows that the anodic Tafel slopes are higher compared to the cathodic Tafel slopes, which means the anodic current increases fast when the potential becomes slightly higher than the OCP. When the lead dodecanoate coating is more protective, this increase will be faster and start at a higher potential.

The values of the inhibition efficiency of the potentiodynamic polarization curves are low compared to the ones obtained by EIS measurements, although they follow the same trend. This could be attributed to the predominant influence of the anodic dissolution process in determining the corrosion rate with Tafel analysis [20].

3.3. Visual comparison of the different deposition methods

Figure 5 shows the optical images of a polished bare lead electrode surface (A) and of lead

dodecanoate modified lead surfaces (B-F). The bare lead surface shows big white spots, which are due to the reflection of the light on the bright lead surface. The optical images of the modified surfaces (Figure 5B - F) show a dull surface covered with small crystals due to the formation of the lead salt. In addition, each modified surface seems to look quite different. Figure 5B shows white areas, which means that unreacted sodium carboxylate reagent is present on the coated surface due to precipitation. Figure 5C and D show rough surfaces and very small surface defects covered with a coating. A possible explanation is the fact that our polished lead surfaces are not smooth enough for a homogeneous coverage. Therefore, attention is given to the use of the initial reduction step, i.e. a pretreatment of the surface. Figure 5E and F show the results of this pretreatment. Figure 5E, using the AMP_IR procedure, shows a dark lead colored surface, which can be explained by assuming the formation of a smooth and fully covering coating on the lead surface. Figure 5F, using the IMM_IR procedure, reveals a smooth surface with almost no defects. The images clearly demonstrate that the surface of the coating is dependent on the used deposition method, which allows us to make assumptions about the corrosion resistance as already predicted by our corrosion measurements.

3.4. Reproducibility of the inhibition layer

Table 4 shows the electrochemical impedance parameters extracted from electrochemical impedance plots of five lead dodecanoate layers on a lead electrode in an ASTM solution deposited using procedure IMM_IR. The inhibition efficiencies of the different layers show a percentage error of 0.35 %. All different lead dodecanoate layers seem to protect and cover the lead surface in a similar way. This means the initial reduction step of the lead surface does not only provide a well-protected surface, but also enhances the reproducibility of our lead dodecanoate coating. We assume the initial reduction step initially levels the lead surface

not only due to the reduction of lead corrosion products, but also due to the redistribution of the freshly polished lead metal. The reduction also activates the lead surface so that an initial faster adsorption of the lead dodecanoate can take place, which states a faster production of the inhibition layer [4]. The lead dodecanoate layer deposited after the reduction process protects the metal much better because we start with a leveled surface, which makes sure that the coating is less susceptible to defects [5].

Summary and conclusions

In this work sodium dodecanoate was deposited as a corrosion protective coating onto a lead surface using three different deposition methods: immobilization of the inhibitor molecules on the lead electrode using cyclic voltammetry, immersion and amperometry. Apart from this, we tested a reduction pretreatment of the lead surface (−1.5 V during 600 seconds) in order to obtain more reproducible coatings. Results show the reduction of the lead surface before the deposition of the layer improves the corrosion resistance of the coating. The corrosion resistance of the coating can be tuned using different deposition methods. The best protecting layers are produced using the immersion method with an initial reduction step (IMM_IR), followed by cyclic voltammetry and eventually amperometry (AMP_IR). The immersion method does not force the formation of lead ions, which allows the formation of well-ordered lead dodecanoate crystals. This is not the case when depositing the layer using voltammetry (CV). Here the electrochemical treatment forces the formation of lead complexes not providing time to form ordered crystals.

Finally, another advantage of using the initial reduction method is the improvement of the reproducibility of the coatings. The reduction levels the polished surfaces and provides each time almost the same initial surface, which determines, to a large extent, the quality of the deposited lead dodecanoate coating on the lead surface.

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Figure captions

Figure 1. Electrochemical impedance plots of a lead dodecanoate modified lead surface (AMP) with and without an initial reduction step of the surface at −1.5 V during 600 seconds recorded in an ASTM D 1384-87 solution.

Figure 2. Electrochemical impedance plots of coated lead electrodes with initial reduction step recorded in ASTM D 1384-87 solution: (A) impedance plot and (B) phase angle plot. The potentiodynamic polarization curves (C) of the deposited dodecanoate coatings are also shown.

Figure 3. Electric circuits used to simulate the electrochemical impedance spectra: (A) circuit for a defective coating and (B) Randles circuit.

Figure 4. The effect of the perturbing voltage (10 - 50 mV) on the corrosion response of a lead dodecanoate coating on a lead surface.

Figure 5. Optical images obtained from a bare lead electrode (A) and lead dodecanoate modified lead electrodes: (B) cyclic voltammetry (procedure CV), (C) amperometry (procedure AMP), (D) immersion (procedure IMM), (E) amperometry with an initial reduction step (procedure AMP_IR) and (F) immersion with an initial reduction step (procedure IMM_IR).

Tables

Table 1. Description of the different modification procedures used to deposit a lead dodecanoate coating on lead electrode surfaces method.

procedure	method	description
CV	cyclic voltammetry	record 5 successive scans in a potential window from −1.3 V to 1.5 V vs SCE with a scan rate of 50 mVs^{-1}
AMP	amperometry	record an amperometric scan at 0.2 V during 2,000 seconds
IMM	immersion	hang the lead surface of the electrode in the solution during 2,000 seconds
AMP_IR	amperometry with initial reduction step	run procedure AMP preceded by a cathodically polarization at −1.5 V during 600 seconds
IMM_IR	immersion with initial reduction step	run procedure IMM preceded by a cathodically polarization at −1.5 V during 600 seconds

Table 2. Potentiodynamic polarization parameters for different lead dodecanoate coatings in an ASTM D 1384-87 solution deposited using different methods in a 0.05 M NaC_{12} solution.

Potentiodynamic polarization parameters					
method	E_{corr} (V/SCE)	i_{corr} (μAcm^{-2})	β_c ($mV\ dec^{-1}$)	β_a ($mV\ dec^{-1}$)	IE (%)
bare lead	−0.558	6.91	60	124	-
amp*(IR)	−0.516	0.937	114	189	86.43
cv	−0.490	0.523	65	118	92.43
imm†(IR)	−0.475	0.00537	81	251	99.92

IR = initial reduction at -1.5 V during 600 seconds

* amperometric deposition at 0.2 V during 2,000 seconds

† deposition using immersion during 2,000 seconds

Table 3. Electrochemical impedance parameters for different lead dodecanoate coatings in an ASTM D 1384-87 solution deposited using different methods in a 0.05 M NaC_{12} solution.

Electrochemical impedance parameters						
method	E_{corr} (V/SCE)	$R_u(\Omega cm^2)$	$R_{pore}(\Omega cm^2)$	$R_{ct}(\Omega cm^2)$	$C_{dl}(\mu F\ cm^{-2})$	IE (%)
bare lead	−0.558	171	123	$3.22 \cdot 10^4$	47.9	-
amp*(IR)	−0.516	298	585	$4.35 \cdot 10^5$	1.7	92.60
cv	−0.490	188	-	$5.21 \cdot 10^6$	0.05	99.38
imm†(IR)	−0.475	287	-	$8.54 \cdot 10^6$	0.04	99.62

IR = initial reduction at -1.5 V during 600 seconds

* amperometric deposition at 0.2 V during 2,000 seconds

† deposition using immersion during 2,000 seconds

Table 4. Fitted electrochemical impedance parameters (EIS) for lead dodecanoate coatings deposited using the immersion method during 2,000 seconds with an initial reduction at -1.5 V for 600 seconds on lead surfaces in an ASTM D 1384-87 solution.

number	E_{corr} (V/SCE)	R_{ct} (Ωcm^2)	IE (%)
bare lead	−0.530	5.12×10^3	-
1	−0.260	5.62×10^5	99.08
2	−0.421	2.28×10^6	99.77
3	−0.565	3.74×10^6	99.86
4	−0.545	4.46×10^6	99.88
5	−0.207	7.09×10^6	99.92